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(21) International Application Number: PCT/US90/01351 (22) International Filing Date: 15 March 1990 (15.03.90) (30) Priority data: 325,724 20 March 1989 (20.03.89) US (71) Applicant: LOCKHEED CORPORATION [US/US]; 4500 Park Granada Boulevard, Calabasas, CA 91399 (US). (72) Inventors: CAMERON, Randy, Edwin ; 15330 Albright Street, #104, Pacific Palisades, CA 90272 (US). LANDIS, Abraham, Lipschitz ; 10935 Canby Avenue, Northridge, CA 91326 (US). (74) Agent: IMAI, Keiichiro; 4500 Park Granada Boulevard, Calabasas, CA 91399 (US).		(81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: CONDUCTIVE POLYMER-MALEIMIDE BLENDS AND METHOD OF PRODUCING SAME (57) Abstract <p>Solution blending of (a) a conductive polymer containing carbon-nitrogen linkages, such as polyaniline, having an organic group or an inorganic group, e.g., derived from an anhydride or an aromatic multisulfonic acid, covalently linked to nitrogen atoms of the polymer and (b) a maleimide, particularly a bismaleimide, e.g., the bismaleimide prepared by reacting 1,3 bis (3 aminophenoxybenzene) with 2 units of maleic anhydride, or a bismaleimide terminated oligomer, in a suitable solvent. On removal of solvent and heating to cure the bismaleimide, a continuous phase blend of the conductive polymer and the bismaleimide is formed, having good electrical conductivity and strength. The solution blend can be applied as a coating on a substrate or can be processed to a powder which can be compressed into parts. The conductive blend can be melted and cured without the evolution of volatiles.</p>		

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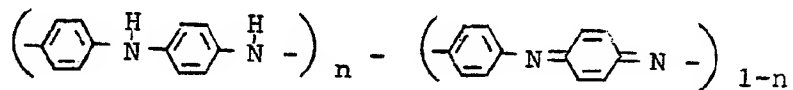
CONDUCTIVE POLYMER-MALEIMIDE BLENDS
AND METHOD OF PRODUCING SAME

BACKGROUND OF THE INVENTION

This application is a continuation-in-part of U. S. Application Serial No. 158,478, filed February 22, 1988, of Stuart I. Yaniger and Randy E. Cameron, and assigned to the same Assignee as the present application.

This invention relates to the production of electrically conductive polymer materials and is particularly concerned with the solution blending of conductive polyaniline and conductive polyaniline derivatives, with maleimide systems, particularly bismaleimide, to produce cured maleimide materials having electrical conductivity, without decreasing the mechanical properties of the maleimide component.

The free-base form of polyaniline is believed to comprise subunits having the formula:



where n is between 0 and 1. The oxidation state of polyaniline referred to as "emeraldine" is believed to have a value of n of about 0.5.

This free-base form of polyaniline is an electrical insulator. Reaction of emeraldine free-base with protonic acids of the form HX, where X is, for example, Cl, causes the polymer to undergo an insulator to conductor transition, as disclosed in A. G. MacDiarmid, et al, Mol. Cryst. Liq.

- 2 -

1 Cryst. 121, 173 (1985). Conductive polyaniline of this type
2 has been employed in batteries as disclosed, for example, in
3 French Patent No. 1,519,729.

4 However, a number of difficulties have been encountered
5 with the prior art materials noted above. Thus, the
6 conductive polyaniline acid salts are, with a few
7 exceptions, insoluble in most solvent media. None of the
8 polyanilines can be melted. The emeraldine free-base and
9 the conductive forms thereof noted above tend to form
10 powders on removal of the solvent. With some effort, films
11 can be cast; however, they are quite fragile and brittle,
12 easily crumbling to form a powder. The conductive acid
13 salts lose their conductivity when exposed to liquid water.
14 This loss is due to deprotonation. The conductivity loss is
15 reversible; treatment of the deprotonated material with
16 protic acids restores the conductivity. Further, conductive
17 regions in an insulating matrix tend toward diffusion. For
18 example, if one makes a conductive trace of polyaniline acid
19 salt on a substrate of emeraldine free-base, the trace
20 remains spatially stable for only a short time, eventually
21 spreading out until the substrate has a constant
22 conductivity throughout.

23 Some of these problems were addressed in U. S.
24 Applications Serial No. 920,474 filed October 20, 1986, of
25 S. I. Yaniger, and Serial No. 013,305 filed February 11,
26 1987, of S. I. Yaniger, et al, both assigned to the same
27 assignee as the present application. In these applications,
28 it is disclosed that Lewis acids, for example, alkylating
29 agents, can be used to make the insulating emeraldine
30 free-base into a conductive polymer salt. Use of proper
31 Lewis acids resulted in conductive polyanilines with the
32 Lewis acid as a side chain. These derivatized polyanilines
33 are more water stable and processable than the prior art
34 emeraldine acid salts. Additionally, no diffusion between
35 "doped" conducting and "undoped" insulating regions was
36 observed.

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1 Thus, in the above U. S. application, Serial No.
2 920,474, a base-type non-conductive polymer, such as
3 polyaniline, can be reacted with, for example, methyl
4 iodide, to form an electrically conductive polymer in which
5 the methyl group is covalently linked to the nitrogen atoms
6 of the polymer.

7 In the above U. S. application, Serial No. 013,305,
8 emeraldine free-base can be reacted with reagents of the
9 form RSO_2Cl , e.g., tosyl chloride, to form an electrically
10 conductive polymer in which the $-\text{SO}_2\text{R}$ groups are covalently
11 linked to the nitrogen atoms of the polymer.

12 U. S. Application Serial No. 158,477 filed February 22,
13 1988, of S. I. Yaniger and R. E. Cameron and assigned to the
14 same assignee as the present application, discloses reaction
15 of a base-type non-conductive polymer, such as polyaniline,
16 with an anhydride, such as tosylic anhydride or benzophenone
17 tetracarboxylic dianhydride, and forming an electrically
18 conductive polymer in which the $-\text{SO}_2\text{R}$ and $-\text{COR}$ groups are
19 covalently linked to the nitrogen atoms of the conductive
20 polymer.

21 In general, however, the conductive polymers of the
22 above applications tend to be brittle, resulting in inferior
23 mechanical properties.

24 It would be desirable to blend the relatively brittle
25 conducting polymer with a flexible polymer to form a blend
26 having both the desired electrical properties and good
27 flexibility.

28 To achieve high electrical conductivity, the proportion
29 of conductive polymer to non-conductive polymer in the blend
30 must be relatively high (e.g., greater than 50%) in order
31 for charge to be transferred effectively between polymer
32 chains. Unfortunately, at high polyaniline loadings, the
33 blend materials tend to phase separate, that is, the
34 polyaniline aggregates into clumps within the non-conductive
35 polymer matrix. These clumps are separated by the matrix
36 material, and the blend thus is an insulator. Further, the

- 4 -

1 mechanical properties of the material suffer upon phase
2 separation. It would be desirable to form blends where the
3 polyaniline is dispersed evenly on a molecular level at all
4 loadings, to thus form a conductive polymer blend.

5 In the above U. S. Application Serial No. 158,478, of
6 which the present application is a continuation-in-part,
7 there is disclosed a conductive polymer blend formed by
8 first reacting a base-type non-conductive polymer containing
9 carbon-nitrogen linkages, such as polyaniline, with a
10 carbonyl anhydride, such as 3,3',4,4'-benzophenone
11 tetracarboxylic dianhydride, to form a conductive polymer
12 containing polyimide-like groups covalently linked to
13 nitrogen atoms of the base-type polymer, mixing such
14 conductive polymer with non-conductive polyimide in a
15 suitable solvent, removing the solvent, and forming a
16 conductive continuous phase blend of the polyimide and the
17 conductive polymer. However, unless the polyimide has a
18 very low melt temperature, the conductive polymer-polyimide
19 blends of the above application are not melt processible and
20 are more useful for making conductive films or fibers than
21 large parts, in which a meltable resin is necessary. In
22 order for a conductive polyaniline to be melt processed or
23 cured with another resin system, such polyaniline must be
24 able to withstand the curing temperature of the other resin
25 system.

26 In U. S. Application Serial No. 226,484, filed August 1,
27 1988, by R. E. Cameron, and assigned to the same assignee as
28 the present application, there is disclosed conductive
29 multisulfonic acid derivatives of polyaniline which are
30 highly thermally stable.

31 Examples of other conductive polymer mixtures are set
32 forth in the following patents.

33 Patent No. 4,526,706 to Upson, et al, discloses a
34 conductive latex coating composition useful in forming
35 conductive layers which comprises a latex having as a
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- 5 -

1 dispersed phase in water hydrophobic polymer particles
2 having associated therewith a polyaniline salt
3 semiconductor. The preferred polymer particles are
4 polyurethane particles, but other polymer particles, such as
5 various acrylate polymers, can be employed.

6 Patent No. 3,766,117 to McQuade discloses a method of
7 preparing an electrodepositable solution of a polyamic acid
8 in an organic solvent, for use in electrodepositing a
9 polyamic acid coating on an electrically conducting
10 substrate. The method comprises preparing a solution of an
11 aromatic polyamic acid in an organic solvent, adding to the
12 polyamic acid solution a base, such as ammonia or an organic
13 amine, e.g., an alkanolamine, and adding water to the base-
14 modified polyamic solution to precipitate at least a portion
15 of the polyamic acid to form a stable electrodepositable
16 dispersion of polyamic acid. A coating of polyamic acid is
17 then electrodeposited from the medium onto a conductive
18 substrate, and the coating is then cured to a polyimide to
19 form an insulation coating.

20 An object of the present invention is the provision of
21 improved electrically conductive polymer materials of the
22 class of conductive polyaniline blended with an imide other
23 than the polyimides of the above U. S. Application Serial
24 No. 158,478.

25 Another object is to provide conductive polymer
26 materials having improved flexibility, mechanical
27 properties, and thermal stability in the form of a
28 continuous phase blend of a conductive polymer, e.g.,
29 conductive polyaniline, and a maleimide, which is capable of
30 melt processing and is particularly applicable for
31 production of large parts.

32 A still further object is to render imides, particularly
33 bismaleimides, conductive by doping with a conductive
34 polymer, such as conductive polyaniline, to produce an
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1 easily processable, highly thermally stable conductive
2 polymer blend.

3 A still further object is to provide novel procedure for
4 blending polyaniline in the solution phase with a maleimide
5 such as bismaleimide, whereby on removal of the solvent, the
6 resulting polymer blend can be processed to yield strong
7 adhesive conductive resins.

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SUMMARY OF THE INVENTION

1 The above objects are achieved and a conductive polymer
2 blend is produced according to the invention by solution
3 blending in a suitable solvent a mixture of (a) an
4 electrically conductive polymer containing carbon-nitrogen
5 linkages, particularly a conductive polyaniline or a
6 polyaniline derivative, and (b) a maleimide, particularly a
7 bismaleimide, removing the solvent, and forming a continuous
8 phase blend of the conductive polymer and the maleimide, as
9 by heating to cure the maleimide.

11 The invention is carried out by first reacting a
12 base-type non-conductive polymer containing carbon-nitrogen
13 linkages, particularly from the family of the polyanilines,
14 with a cation donor compound capable of covalently binding
15 to the nitrogens of the polymer, such as a carbonyl or
16 sulfonyl anhydride, to thereby form an electrically
17 conductive polymer, e.g., a derivatized polyaniline having
18 an organic or inorganic group covalently linked to nitrogen
19 atoms of the base-type polymer, e.g., as described in the
20 above U. S. Application Serial No. 158,477 of S. I. Yaniger,
21 et al.

22 The conductive polymer so formed is mixed with a
23 maleimide, particularly a bismaleimide, e.g., in certain
24 ranges of proportions as described hereinafter, in a
25 suitable solvent, such as N-methyl pyrrolidone (NMP), to
26 form a melt processible blend of the two components in the
27 solution phase. Upon removal of the solvent, the mixture
28 forms a continuous phase blend, the blended materials
29 resulting in an electrically conductive resin which is
30 strong and can be used as the matrix material in a
31 non-metallic conductive composite, e.g., for fabrication of
32 large parts, such as aircraft components. The blends of the
33 present application are thermosetting in that they melt and
34 cure to an insoluble part.

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- 8 -

1 Another important advantage of the conductive
2 polyaniline blends of the present application is that the
3 bismaleimide thereof cures without giving off volatiles and
4 without decomposing the polyaniline, whereas the curing of
5 the polyimide in the conductive polyaniline-polyimide blends
6 of above U. S. Application Serial No. 158,478 evolves
7 volatiles.

8 If desired, in the above procedure, the electrically
9 conductive polymer, e.g., conductive polyaniline, can be
10 formed in situ, during solution blending with the maleimide
11 component, by incorporating in the solvent solution the
12 non-conductive polymer, e.g., polyaniline, and the cation
13 donor compound for reaction with such non-conductive
14 polymer, to form the resulting conductive polymer, in
15 solution with the maleimide component.

16 Thus, the present invention discloses a technique for
17 increasing the electrical conductivity of a maleimide,
18 particularly bismaleimide, without materially adversely
19 affecting, or without decreasing, the mechanical properties
20 thereof.

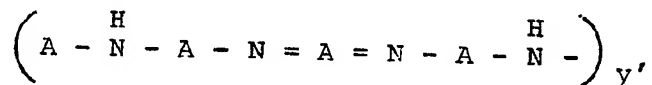
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- 9 -

DETAILED DESCRIPTION OF THE INVENTIONAND PREFERRED EMBODIMENTSConductive Polymer Component

In preferred practice, a base-type non-conductive polymer containing carbon-nitrogen linkages is first reacted with a cation donor compound to form a polymer salt in which a covalent bond is formed between the nitrogens of the polymer and such donor cation.

A preferred form of non-conductive polymer can be represented as follows:



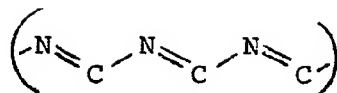
where A is a carbon-containing group, such as aryl, particularly the benzene ring, as in polyaniline, and including naphthyl and biphenyl, and substituted benzene, naphthyl or biphenyl groups, such as the alkyl substituted derivatives, e.g., 2-methyl biphenyl, butyl naphthalene, 2-methyl aniline, and aryl substituted derivatives, e.g., beta phenyl naphthalene and beta tolyl naphthalene; and y is an integer ranging from about 1 to about 1,000, e.g., about 10 to about 100.

Thus, the above non-conductive polyaniline family of polymers can be further characterized as consisting of polyaniline, its naphthyl and biphenyl derivatives, and alkyl and aryl substituted polyaniline and its alkyl and aryl substituted naphthyl and biphenyl derivatives.

The preferred non-conductive polymer containing carbon-nitrogen linkages is the basic polymeric starting material, polyaniline emeraldine free-base (PFB).

Other polymeric starting materials can include other non-conductive base-type polymers containing carbon atoms linked to nitrogen, such as cyanogen polymer containing the recurring unit:

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The starting materials of the invention can also include non-conductive mixtures and blends of the above polymers, and copolymers of the above polymers and other polymers, such as a blend of polyaniline and polymethylmethacrylate, and polymer alloys, such as polybenzimidazole-polyimide alloys, containing carbon-nitrogen groups.

Thus, the term "non-conductive polymer" as employed herein is intended to denote any of the above homopolymer or copolymer materials.

The invention will be described hereinafter, however mostly in terms of the use of the preferred non-conductive free-base polyaniline as polymeric starting material. This is a high polymer having a molecular weight of the order of 50,000 to 80,000. Lower molecular weight forms of polyaniline can also be employed, such as an oligomer of polyaniline containing 8 sub-units and having a molecular weight of about 800 to 900.

The non-conductive polymer, e.g., polyaniline, can be reacted with any dopant which is effective to increase the electrical conductivity of the polymer. Thus, for example, the free-base polyaniline can be reacted with protonic acids, such as HX, where X is a halogen, such as Cl, to convert the insulator to a conductor, as disclosed in the above MacDiarmid reference.

However, the preferred conductive polymers are those prepared by reacting the non-conductive polymer containing carbon-nitrogen linkages, such as polyaniline, with a cation donor compound capable of covalently binding to the nitrogens of such polymer to form an electrically conductive polymer. Thus, the resulting conductive polymer has an organic or inorganic group covalently linked to nitrogen

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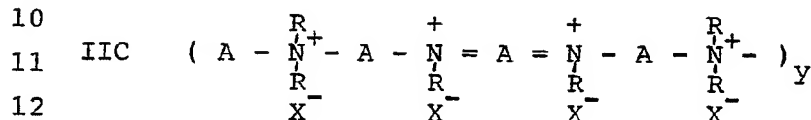
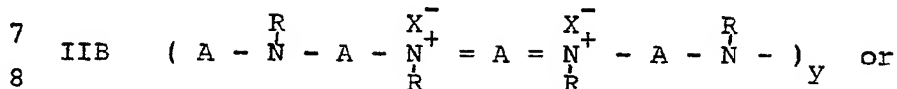
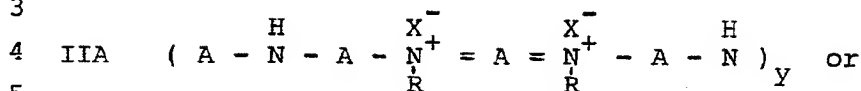
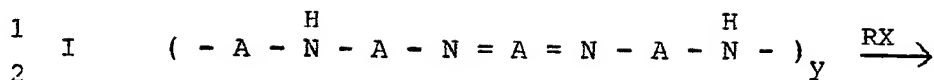
1 atoms of the polymer and an anion associated with such
2 nitrogen atoms to form a polymer salt.

3 Such conductive polymers and their method of formation
4 are described in the above-noted applications. Thus, for
5 example, the free-base polyaniline can be treated and
6 reacted with an R^+ donor compound, such as RX , R_3OX , R_2SO_4 ,
7 $R'SO_2Cl$, or $R''SiQ$, where R , $R'SO_2$ or $R''Si$ is a group which
8 readily forms a covalent bond with nitrogen, and wherein R ,
9 R' and R'' each can be alkyl containing from 1 to 20 carbon
10 atoms, e.g., methyl, ethyl and the like, and aryl, e.g.,
11 p-toluene sulfonyl (tosyl), benzyl, tolyl, xylyl, and other
12 aromatic moieties, and X is an anion such as halogen, e.g.,
13 Cl^- , I^- or Br^- ; PF_6^- , $SbCl_6^-$, and substituted and
14 unsubstituted benzene sulfonate, and the like, and Q is a
15 halogen, such as Cl . The above reaction forms a conductive
16 polymer salt.

17 Thus, the reactant which forms a covalent chemical bond
18 with the nitrogen of the polyaniline free-base or equivalent
19 polymer noted above, can be, for example, one of the above
20 R^+ donor compounds, such as an alkyl halide, wherein the
21 alkyl group can contain from 1 to 20 carbon atoms, such as
22 methyl iodide, or dimethylsulfate.

23 The reaction for converting the base-type non-conductive
24 polymer to a conductive polymer can be represented as
25 follows, where, for example, RX is the R^+ donor compound:
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14 where A and y are as defined above.

15 According to another preferred embodiment, as disclosed
 16 in the above U. S. Application Serial No. 158,477, base-type
 17 non-conductive polymers containing carbon-nitrogen linkages,
 18 particularly from the family of polyaniline, can be
 19 converted to conductive polymers by reacting the
 20 non-conductive polymer with an anhydride, such as
 21 $R-SO_2-O-SO_2R'$, $R-CO-O-CO-R'$, or $R-CO-O-SO_2R'$, or mixtures
 22 thereof, where R and R' are alkyl or aryl, e.g., tosylic
 23 anhydride, benzophenone tetracarboxylic dianhydride, or
 24 o-sulfobenzoic anhydride, according to the general reaction
 25 shown above, and forming an electrically conductive polymer
 26 in which the SO_2R and COR groups are covalently linked to
 27 the nitrogen atoms of the conductive polymer and the anion
 28 of the conductive polymer is the SO_3R' or O_2CR' group.

29 According to still another preferred embodiment as
 30 disclosed in above U. S. Application Serial No. 226,484,
 31 filed August 1, 1988, by R. E. Cameron, base-type
 32 non-conductive polymers containing carbon-nitrogen link-
 33 ages, particularly from the family of polyaniline, are

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1 converted to conductive polymers of high thermal stability,
2 by reacting the non-conductive polymer with a multiprotic
3 acid in the form of an aromatic multisulfonic acid, e.g.,
4 having the formula $R(SO_3H)_n$, where R is aryl, such as
5 benzene or naphthalene, or their substituted derivatives,
6 and n is an integer of at least 2, preferably 2 to 4, or
7 mixtures thereof, such as m-benzene disulfonic acid, to form
8 a polymer salt in which the $-SO_3H$ groups are covalently
9 linked to the nitrogens of the polymer through the hydrogen
10 bond.

11 The molar proportions of cation donor compound to
12 non-conductive, e.g., nitrogen-containing polymer free-base,
13 can be varied but is sufficient to increase the electrical
14 conductivity of the polymer. Thus, for example, in the case
15 of the above donor compounds RX , R_3OX , R_2SO_4 , $R'SO_2Cl$ and
16 R_3SiQ and the anhydrides, the molar proportions of donor
17 compound to nitrogen-containing polymer can range from about
18 0.01 to about 2 cation groups, e.g., SO_2R^+ or COR^+ groups in
19 the case of the anhydride, per nitrogen, and in the case of
20 polyaniline, such molar proportions can range from about
21 0.01 to about 8, per polymer repeat unit. Where an aromatic
22 multisulfonic acid is employed as cation donor compound, a
23 range of proportions of about 1/16 to about 2 moles of
24 multisulfonic acid per nitrogen of each polymer unit is
25 employed and, in the case of polyaniline, from about 1/8 to
26 about 2 moles of multisulfonic acid, for every 2 aniline
27 units in the polyaniline chain.

28 The reaction can be carried out as a heterogeneous
29 reaction wherein the polymer starting material is not
30 dissolved but is reacted directly with the cation donor
31 compound, e.g., anhydride, or the polymer starting material,
32 such as polyaniline non-conductive free-base, can be
33 dissolved in a suitable solvent which does not react
34 irreversibly with such donor compound, e.g., N-methyl
35 pyrrolidone, dimethylsulfoxide (DMSO), dimethylformamide
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- 14 -

1 (DMF), formic acid, dimethylacetamide (DMAC), acetonitrile,
2 tetrahydrofuran (THF), and pyridine.

3 The reaction is generally carried out at about ambient
4 or room temperature, e.g., 20 - 25° C., or at higher or
5 lower temperatures.

6 The rate of reaction can range widely, depending on the
7 particular cation donor compound reactant employed. Thus,
8 the reaction rate can range from almost instantaneous to
9 several hours or longer.

10 The conductivity of the resulting conductive polymers,
11 e.g., conductive polyaniline, can be varied by reducing or
12 increasing the number of covalently linked side chains on
13 the nitrogen atoms, as by controlling the degree of
14 completeness of the reaction and/or by varying the types of
15 cation donor compound employed in producing such side chains
16 on the polymer.

17 The disclosures of the above applications and the
18 MacDiarmid reference are incorporated herein by reference
19 with respect to the conductive polymer component of the
20 present invention and its method of preparation.

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22 Maleimide Component

23 The maleimide component which is blended with the above
24 conductive polymer according to the invention can have a
25 single terminal maleimide unit but is preferably a
26 bismaleimide capped at opposite ends of the molecule with a
27 maleimide unit. The maleimide component can be in the form
28 of a monomer or an oligomer, preferably a bismaleimide
29 terminated oligomer.

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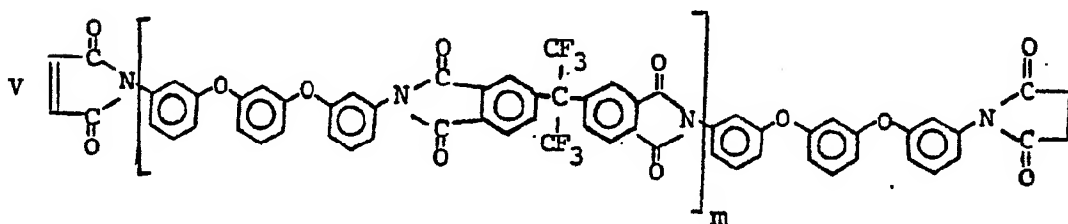
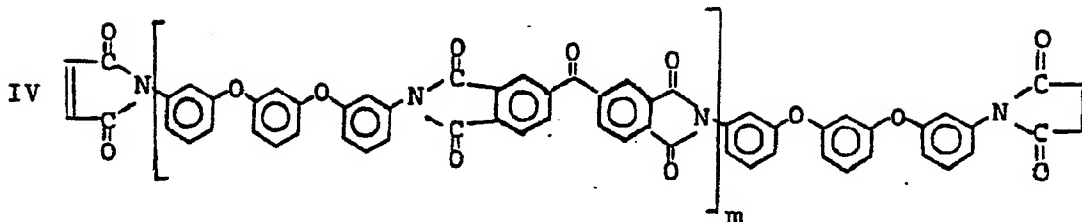
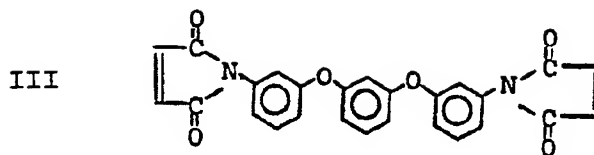
31 Examples of maleimide components which can be employed
32 according to the invention are as follows:

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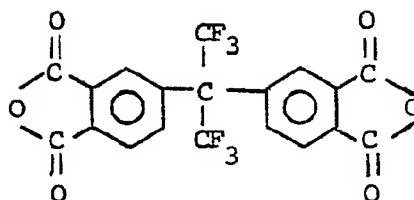
where m is an integer of from 1 to about 10, preferably 1 to about 4.

The BMI (bismaleimide) of formula III is known and can be made by reacting 1,3 bis (3-aminophenoxybenzene (APB)) and two units of MI (maleimide).

The BMI of formula IV is known and can be made by reacting 10 units of APB and 10 units of benzophenonetetracarboxylic dianhydride (BTDA) capped by 2 units of MI.

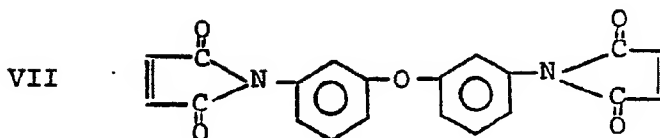
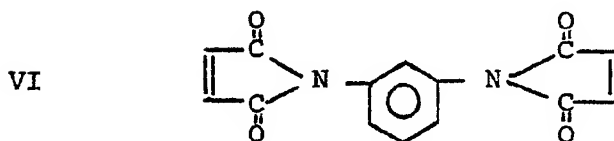
The BMI of formula V can be made in known manner by reacting 10 units of APB and 10 units of the anhydride marketed as 6FDA and having the formula:

- 16 -



capped by 2 units of MI.

Examples of additional BMI's are as follows:



The conductive polymer can be blended in a wide range of proportions with non-conductive maleimide component, generally ranging from about 1 to about 99% conductive polymer to 1 to about 99% non-conductive maleimide component, e.g., bismaleimide, by weight of the mixture.

- 17 -

1 Particularly to obtain higher conductivity, it is preferred
2 to employ about 50 to about 99% conductive polymer and about
3 1 to about 50% non-conductive maleimide component, by
4 weight. Such blending can be carried out by mixing the
5 conductive polymer with non-conductive maleimide component
6 in a suitable solvent, such as N-methyl pyrrolidone. Other
7 solvents which can be employed are noted above. If desired,
8 the reaction of the non-conductive base-type polymer, such
9 as polyaniline, with the appropriate cation donor compound,
10 e.g., anhydride, can be carried out in a suitable solvent,
11 such as N-methyl pyrrolidone, and the maleimide component
12 can then be added to the resulting reaction mixture
13 containing the resulting conductive base-type polymer.

14 Instead of blending the derivatized conductive polymer,
15 e.g., polyaniline, with preformed maleimide, e.g.,
16 bismaleimide, component, the non-conductive polyaniline can
17 be mixed with cation donor compound, e.g., an anhydride, in
18 solvent solution with maleimide component, and the reaction
19 to form the conductive polymer, e.g., conductive
20 polyaniline, takes place in situ during blending thereof
21 with the maleimide component. Alternatively, the maleimide
22 component, or both the conductive polymer and maleimide
23 components, can be formed in situ during blending.

24 When employed to form a coating, the resulting blend in
25 which the conductive polymer and maleimide components are
26 completely soluble is applied to any suitable substrate,
27 either conductive or non-conductive, such as glass, quartz,
28 metal or plastic, and the solvent is evaporated. The
29 resulting film is cured by heating at elevated temperature
30 for a suitable time period. A tough, flexible film in the
31 form of a continuous phase blend of the conductive polymer
32 and the maleimide component is obtained, which has high
33 electrical conductivity. The proportions of base-type
34 polymer and maleimide component in the continuous phase
35
36

- 18 -

1 blend forming the conductive film is the same as that noted
2 above in preparing the solutions of the blends. The blended
3 polymer also has the good mechanical properties of the
4 maleimide component while having the good electrical
5 conductivity properties of the conductive base-type polymer,
6 such as conductive polyaniline. The continuous single-phase
7 blends of the conductive polymer and non-conductive
8 maleimide component produced according to the invention do
9 not separate out upon forming a film from the blend.

10 Further, upon removal of solvent, the resulting polymer
11 blend can be melt processed to yield strong adhesive resins

12 Instead of forming a blend of the two components and the
13 blend used to form a coating, the conductive polymer and
14 maleimide component blend can be processed to a powder.
15 This can be achieved, e.g., by blending the non-conductive
16 polymer, e.g., polyaniline, in solvent solution, e.g., NMP,
17 with maleimide component, particularly bismaleimide, and
18 adding a cation donor compound, such as benzene disulfonic
19 acid for reaction with the polyaniline to form conductive
20 polymer. The resulting blend of both components is
21 precipitated out of solution by adding a precipitating
22 agent, such as hexane, toluene, or a mixture thereof, to the
23 solution blend. The precipitate can be filtered, and the
24 resulting powder can be pressed or molded into a thermoset
25 part and cured of elevated temperature.

26

27 Example 1

28 10 grams of PA (polyaniline) emeraldine free-base is
29 dissolved into 250 ml of NMP. To this solution is added 10
30 grams of the BMI of formula III above. 6.5 grams of
31 m-benzene disulfonic acid is added to the resulting
32 solution. The solution turns green. This solution contains
33 about 50% of conductive PA and about 50% of the BMI, by
34 weight of the mixture.

35

36

- 19 -

1 The NMP is evaporated from the resulting solution or
2 blend, and a film is cast from the resulting conductive PA
3 and BMI blend on a glass substrate. The resulting film is
4 heated at 180° C. in air for 3 hours. The cured film is
5 electrically conductive and strong.

6
7 Example 2

8 The solution or blend of conductive PA and BMI is formed
9 as in Example 1. Such solution is added dropwise to 500 ml
10 of a 50-50 mixture of hexane-toluene.

11 A green precipitate is formed, which is filtered from
12 the reaction mixture. The filtered precipitate is washed
13 with excess hexane. The resulting dry powder can then be
14 pressed into pellets or parts. Such compressed pellets or
15 parts are cured by heating in air, argon or nitrogen at
16 180° C. for 4 hours. Since the BMI melts prior to curing at
17 180° C., the resulting electrically conductive parts have
18 good mechanical properties.

19 The table below shows the relationship between time of
20 curing and conductivity, for curing of the compressed
21 pellets.

22
23 TABLE

24	25 <u>TIME OF CURING (HOURS)</u>	26 <u>ELECTRICAL CONDUCTIVITY (S/cm)</u>
27	0	10^{-1}
28	1	10^{-2}
29	2	$10^{-2.5}$
30	3½	$10^{-2.5}$

31 The above table shows that there is an initial decrease
32 in conductivity during the first 2 hours of curing, but once
33 the material has cured, e.g., after about 3 hours, there is
34 no longer any further drop in electrical conductivity, as

- 20 -

1 shown by the same value of conductivity for 3½ hours of
2 curing as for 2 hours of curing. This shows that although
3 there is an initial drop in electrical conductivity of the
4 resin blend, e.g., due to binding of the BMI to the
5 polyaniline amine groups, following curing, the cured resin
6 is still conductive and the electrical conductivity remains
7 constant. This indicates that the conductive polyaniline of
8 the blend does not decompose during or after curing.

9 If a higher electrical conductivity for the cured resin
10 blend is desired, a larger proportion of the conductive
11 polyaniline polymer is employed in the blend of conductive
12 polymer and BMI, e.g., 75% conductive polyaniline and 25%
13 BMI, by weight of the mixture.

14 15 Example 3

16 The procedure of Example 1 is followed except employing
17 o-sulfobenzoic anhydride or p-toluenesulfonic anhydride,
18 respectively, in place of m-benzene disulfonic acid and in
19 the same amount as the latter cation donor compound for the
20 PA.

21 Results similar to Example 1 are obtained.

22 23 Example 4

24 The procedure of Example 1 is carried out using
25 isopropyl iodide or $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{Cl}$, respectively, as cation
26 donor compound for the PA in place of m-benzene disulfonic
27 acid, and in the same amount thereof.

28 Results similar to Example 1 are obtained.

29 30 Example 5

31 The procedure of Example 1 is followed except employing
32 dimethyl sulfate in the same amount as the m-benzene
33 disulfonic acid.

34 Results similar to Example 1 are obtained.

- 21 -

1 Example 6

2 The procedure of Example 1 is carried out except using
3 the hydrogen ion form of Nafion, a multisulfonic acid
4 derivative of perfluorinated polymer, marketed by DuPont,
5 instead of m-benzene disulfonic acid and in the same amount.

6 Results similar to Example 1 are obtained.
7

8 Example 7

9 The procedure of Example 1 is carried out, except using
10 the BMI of formula IV above and in the same amount as the
11 BMI of formula III.

12 Results similar to Example I are obtained.
13

14 Example 8

15 The procedure of Example 1 is carried out, except using
16 the BMI of formula V above and in the same amount as the BMI
17 of formula III.

18 Results similar to Example I are obtained.
19

20 Example 9

21 The procedure of Example 1 is repeated, except using 5
22 grams of PA free-base and 15 grams of the BMI component to
23 form a solution blend containing about 25% of conductive PA
24 and about 75% of the BMI, by weight of the mixture.
25

26 The electrically conductive polymer blends of the
27 invention have utility in the production of conductive
28 composites, electronic components, electrical conductors,
29 electrodes, batteries, switches, electrical shielding
30 material, resistors, capacitors, and the like.
31
32
33
34
35
36

- 22 -

1 From the foregoing, it is seen that the invention
2 provides a novel class of conductive polymer materials which
3 can be readily cast into tough, flexible conductive films,
4 by solution blending conductive, preferably
5 nitrogen-containing, polymers, such as conductive
6 polyaniline, with a maleimide component, particularly a
7 bismaleimide. The resulting resin blend increases the
8 electrical conductivity of the maleimide component without
9 decreasing its mechanical integrity. The result is a
10 conductive resin of superior strength, toughness,
11 flexibility and processibility. Due to the melting followed
12 by curing of the BMI when blended with the conductive
13 polyaniline, the conductive blend can be melted and cured
14 without the evolution of volatiles. No polyaniline
15 decomposition is seen with these materials.

16 While particular embodiments of the invention have been
17 described for purposes of illustration, it will be
18 understood that various changes and modifications within the
19 spirit of the invention can be made, and the invention is
20 not to be taken as limited except by the scope of the
21 appended claims.

- 23 -

WHAT IS CLAIMED IS:

1. The process for producing a conductive polymer blend which comprises:

solution blending in a suitable solvent a mixture of (a) a conductive polymer containing carbon-nitrogen linkages, and (b) a maleimide,

removing said solvent, and

forming a conductive continuous phase blend of said conductive polymer and said maleimide.

2. The process of claim 1, said conductive polymer being selected from the group consisting of conductive polyaniline, its naphthyl and biphenyl derivatives, and alkyl and aryl substituted polyaniline and its alkyl and aryl substituted naphthyl and biphenyl derivatives.

3. The process of claim 1, said conductive polymer having an organic or inorganic group covalently linked to nitrogen atoms of said polymer.

4. The process of claim 2, wherein said conductive polymer has an organic group derived from an anhydride or an aromatic multisulfonic acid covalently linked to the nitrogen atoms of said polymer.

5. The process of claim 2, wherein said conductive polymer is polyaniline and said conductive polyaniline has an organic group derived from an anhydride or an aromatic multisulfonic acid covalently linked to the nitrogen atoms of said polyaniline.

- 24 -

6. The process of claim 1, wherein said maleimide is a bismaleimide or a bismaleimide terminated oligomer.

7. The process of claim 5, wherein said maleimide is a bismaleimide terminated oligomer, employing about 1 to about 99% of said conductive polymer and about 1 to about 99% of said maleimide, by weight of the mixture.

8. The process of claim 1, including heating said continuous phase blend and curing said maleimide.

9. A process for producing a conductive polymer blend which comprises:

5 reacting a base-type non-conductive polymer containing carbon-nitrogen linkages selected from the group consisting of polyaniline, its naphthyl and biphenyl derivatives, and alkyl and aryl substituted polyaniline and its alkyl and aryl substituted naphthyl and biphenyl derivatives, with a compound capable of converting said non-conductive polymer to a conductive polymer, and forming
10 said conductive polymer having an organic or inorganic group covalently linked to nitrogen atoms of said polymer,

solution blending a maleimide with said conductive polymer in a suitable solvent,

removing said solvent, and

15 forming a conductive continuous phase blend of said conductive polymer and said maleimide.

- 25 -

10. The process of claim 9, wherein said reaction to form said conductive polymer is carried out in situ during solution blending with said maleimide.

11. The process of claim 9, wherein said maleimide is a bismaleimide or a bismaleimide terminated oligomer.

12. The process of claim 9, wherein said compound is a carbonyl anhydride or a sulfonyl anhydride, and forming anhydride groups covalently linked to nitrogen atoms of said polymer.

13. The process of claim 9, wherein said compound is an aromatic multisulfonic acid.

14. The process of claim 9, wherein said compound is selected from the group consisting of RX , R_3OX , R_2SO_4 , $R'SO_2Cl$ and $R''SiQ$, where R , $R'SO_2$ or $R''Si$ is a group which forms a covalent bond with nitrogen and wherein R , R' and R'' is alkyl containing from 1 to 20 carbon atoms or aryl, and Q is a halogen.

15. The process of claim 9, employing about 1 to about 99% of said conductive polymer and about 1 to about 99% of said maleimide, by weight of the mixture.

16. The process of claim 15, wherein said polymer is polyaniline and said maleimide is bismaleimide or a bismaleimide terminated oligomer.

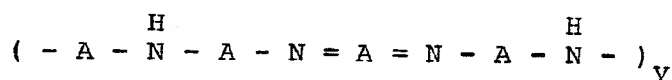
- 26 -

17. The process of claim 16, wherein said compound is a carbonyl anhydride or a sulfonyl anhydride, and forming anhydride groups covalently linked to nitrogen atoms of said polymer, and including heating said continuous phase blend.

18. The process of claim 16, wherein said compound is an aromatic multisulfonic acid, and forming $-SO_3H$ groups covalently linked to nitrogen atoms of said polymer through the hydrogen bond on the nitrogen atoms, and including heating said continuous phase blend.

19. A blend of (a) a conductive polymer containing carbon-nitrogen linkages and (b) a maleimide, in a suitable solvent.

20. The blend of claim 19, wherein said conductive polymer is derived from a polymer having the formula:



where A is aryl and y is an integer of from about 1 to about 1,000.

21. The blend of claim 19, said conductive polymer selected from the group consisting of conductive polyaniline, its naphthyl and biphenyl derivatives, and alkyl and aryl substituted polyaniline and its alkyl and aryl substituted naphthyl and biphenyl derivatives, and (b) a maleimide.

- 27 -

22. The blend of claim 21, employing about 1 to about 99% of said conductive polymer and about 1 to about 99% of said maleimide, by weight of the mixture.

23. The blend of claim 21, said conductive polymer having an organic or inorganic group covalently linked to nitrogen atoms of said polymer.

24. The blend of claim 21, wherein said conductive polymer is conductive polyaniline, and said conductive polyaniline has an organic group derived from an anhydride or an organic multisulfonic acid covalently linked to the nitrogen atoms of said polyaniline.

25. The blend of claim 21, wherein said maleimide is a bismaleimide or a bismaleimide terminated oligomer.

26. The blend of claim 24, wherein said maleimide is a bismaleimide or a bismaleimide terminated oligomer, employing about 1 to about 99% of said conductive polymer and about 1 to about 99% of said maleimide, by weight of the mixture.

27. An electrically conductive solid polymer material, comprising a continuous phase blend of (a) a conductive polymer containing carbon-nitrogen linkages selected from the group consisting of conductive polyaniline, its naphthyl and biphenyl derivatives, and alkyl and aryl substituted polyaniline and its alkyl and aryl substituted naphthyl and biphenyl derivatives, and (b) a maleimide, said polymer material containing about 1 to about 99% of said conductive polymer and about 1 to about 99% of said maleimide, by weight.

- 28 -

28. The electrically conductive polymer material of claim 27, said conductive polymer having an organic or inorganic group covalently linked to nitrogen atoms of said polymer.

29. The electrically conductive polymer material of claim 27, wherein said conductive polymer has an organic group derived from an anhydride or an aromatic multisulfonic acid covalently linked to the nitrogen atoms of said polymer.

30. The electrically conductive polymer material of claim 27, wherein said polymer is polyaniline, and said conductive polyaniline has an organic group derived from a multisulfonic acid covalently linked to the nitrogen atoms of said polyaniline.

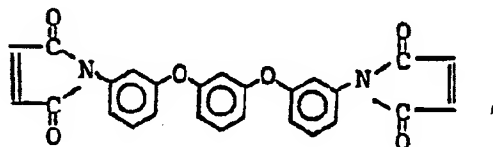
31. The electrically conductive polymer material of claim 27, wherein said polymer is polyaniline, and said conductive polyaniline has an organic group selected from the class consisting of R, R'SO₂ and R₃Si covalently linked to the nitrogen atoms of said polyaniline, where R, R' and R" is alkyl or aryl.

32. The electrically conductive polymer material of claim 27, wherein said maleimide is a bismaleimide or a bismaleimide terminated oligomer.

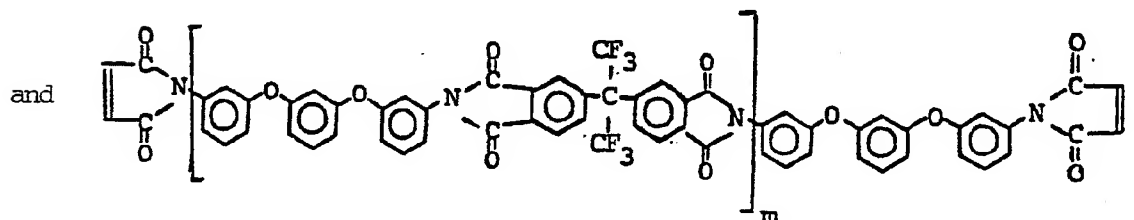
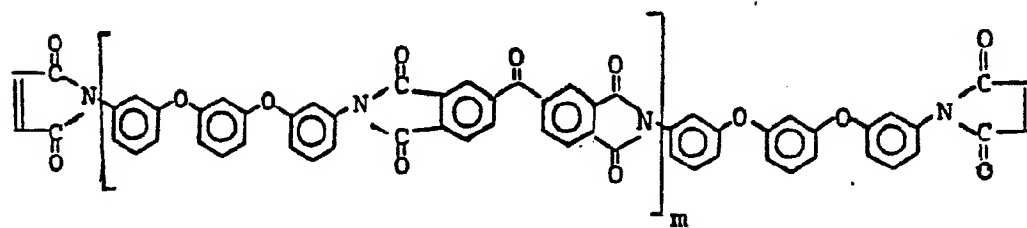
33. The electrically conductive polymer material of claim 30, wherein said maleimide is a bismaleimide or a bismaleimide terminated oligomer.

- 29 -

34. The electrically conductive polymer material of claim 30, wherein said maleimide is a compound selected from the group having the following formulae:



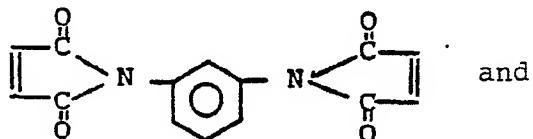
5



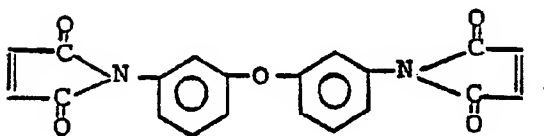
where m is an integer of from 1 to about 10.

- 30 -

35. The electrically conductive polymer material of claim 30, wherein said maleimide is a compound selected from the group having the following formulae:



and



5

INTERNATIONAL SEARCH REPORT

International Application No. **PCT/US90/01351**

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶

According to International Patent Classification (IPC) as to both National Classification and IPC/20
IPC (5): C08J 7/14; C08L 79/02; 79/08; H01B 1/12; 1/20
U.S. CL: 252/500; 520, 422, 436, 540

II. FIELDS SEARCHED

Minimum Documentation Searched ⁷	
Classification System	Classification Symbols
U.S.	252/500; 525/422, 436, 540

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched ⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹

Category [*]	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	FR, A, 1519729 (Centre Nationale De La Recherche Scientifique), see page 1 and Examples 1 and 2.	1-34
A	US, A, 3,766,117 (McQuade) 16 October 1973, see claim 1.	1-34
A	Mol. Cryst. Liq Cryst., Volume 121 1985 (U.S.A.) Alan G. MacDiarmid, "polyaniline: Interconversion of Metallic And Insulating Forms", page 173, see the entire document.	1-34
X Y	US, A, 4,692,225 (Witucki) 08 September 1987, see column 2, lines 20-29; column 4, lines 53-59	19-34 1-18
A	US, A, 4,798,685 (Yaniger) 17 January 1989 see the entire document.	1-34
A	US, A, 4,526,706 (Upson) 02 July 1985, see the abstract.	1-34
A	US, A, 4,806,271 (Yaniger) 21 February 1989, see the entire document.	1-34
P,A	US, A, 4,851,487 (Yaniger) 25 July 1989, see the entire document.	1-34
P,Y	US, A, 4,855,361 (Yaniger) 08 August 1989, see column 3, lines 5 to 23.	1-18

^{*} Special categories of cited documents: ¹⁰

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

14 MAY 1990

International Searching Authority

TSA/US

Date of Mailing of this International Search Report

24 JUL 1990

Signature of Authorized Officer

Alan L. Lieberman
ALLAN L. LIEBERMAN